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(54) **New peroxide curable fluoroelastomers, particularly suitable for manufacturing O-rings.**

(57) New fluoroelastomers are described, having iodine atoms in terminal position and monomeric units in the chain deriving from an iodinated olefin of formula:

$CHR=CH-Z-CH_2CHR-I$ (I)

wherein: R is -H or $-CH_3$; Z is a (per)fluoroalkylene radical C_1-C_{18}, linear or branched, optionally containing one or more ether oxygen atoms, or a (per)fluoropolyoxyalkylene radical.

These products, upon peroxide curing, require extremely short post-curing treatments (around 30-60 minutes at 180°-230°C) and are characterized by compression set values lower than 25% (measured on O-rings at 200°C for 70 hours according to ASTM Standard D395 Method B).

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The present invention relates to new peroxide curable fluoroelastomers particularly suitable for manufacturing O-rings.

Various types of fluoroelastomers are known in the art, widely used in all those fields where superior elastic properties associated with high thermochemical stability are required. For a wide survey on such products see for instance "Ullmann's Encyclopedia of Industrial Chemistry", vol. A-11, pag. 417-429 (1988, VCH Verlagsgesellschaft).

It is also known that for manufacturing sealing elements, particularly O-rings, it is necessary to use elastomers endowed with particularly low compression set values. In fact, O-ring sealing effectiveness is as better as the article, upon compression, is able to recover initial dimensions. Since the fluoroelastomers are used in a wide temperature range, compression set values should be low not only at low temperatures, but also at high temperatures. Compression set values (measured at 200°C for 70 hours, according to ASTM Standard D395, Method B) lower than 25% are generally required. More particularly, military specifications (MIL-R-83248B) asks for O-rings having a maximum compression set value of 20% (measured at 200°C for 70 hours as well).

Fluoroelastomers which can meet such requirements are those curable ionically, which need addition of curing agents (for instance polyhydroxy compounds, such as Bisphenol AF or Bisphenol A), of suitable accelerators (for instance ammonium, phosphonium or amino-phosphonium salts), and of divalent metal oxides and/or hydroxides (for instance MgO, $Ca(OH)_2$). Elastomers of this type are described for instance in patent application EP-525,685. However, ionic curing shows some drawbacks, among which the fact that a post-curing treatment is needed, generally carried out at 200°-260°C for 12-24 hours, in order to complete curing, and to eliminate volatile by-products, so as to improve and stabilize mechanical and elastic properties. This implies a remarkable increase in processing times and costs and therefore strongly limits the possibilities of large scale production.

As described in US Patent 4,243,770, fluoroelastomers can be crosslinked also by means of peroxides. To such purpose it is necessary to carry out the polymerization in the presence of suitable iodinated chain transfer agents, which introduce into the macromolecules iodine atoms in terminal position: in the presence of radicals deriving from a peroxide said iodine atoms act as cure sites in consequence of homolitic breakage of the C-I bonds. Fluoroelastomers of this type generally do not require long post-curing treatments: in some cases it is sufficient a post-curing in air at about 200°-230°C for 1-4 hours. However, such products do not meet the specifications indicated above for O-ring manufacturing: the compression set value is indeed usually high, at least equal to 28-30% or higher.

The Applicant has now found a new class of fluoroelastomers as defined hereinunder, which, upon peroxide curing, need extremely short post-curing treatments (around 30-60 minutes at 180°-230°C) and are characterized by compression set values lower than 25% (measured on O-rings at 200°C for 70 hours according to ASTM Standard D395 Method B).

Therefore, a first object of the present invention are peroxide curable fluoroelastomers, having iodine atoms in terminal position, and monomeric units in the chain deriving from an iodinated olefin of formula:

$$CHR=CH\text{-}Z\text{-}CH_2CHR\text{-}I \qquad (I)$$

wherein: R is -H or $-CH_3$; Z is a C_1-C_{18} (per)fluoroalkylene radical, linear or branched, optionally containing one or more ether oxygen atoms, or a (per)fluoropolyoxyalkylene radical.

Further objects of the present invention are the iodinated olefins of formula (I), and the preparation process thereof, as described hereinunder.

As regards formula (I), Z is preferably a C_4-C_{12} perfluoroalkylene radical, or a (per)-fluoropolyoxyalkylene radical of formula:

$$-(Q)_p\text{-}CF_2O\text{-}(CF_2CF_2O)_m(CF_2O)_n\text{-}CF_2\text{-}(Q)_p\text{-} \qquad (II)$$

wherein: Q is a C_1-C_6, preferably C_1-C_3, alkylene or oxyalkylene radical; p is 0 or 1; m and n are numbers such that the m/n ratio is from 0.2 to 5 and the molecular weight of said (per)fluoropolyoxyalkylene radical is from 400 to 10,000, preferably from 500 to 1,000. Preferably, Q is selected from: $-CH_2O-$; $-CH_2OCH_2-$; $-CH_2-$; $-CH_2CH_2-$.

The olefins of formula (I) can be prepared starting from compounds of formula I-Z-I according to the following process:

(1) adding ethylene or propylene to a compound of formula I-Z-I, thus obtaining a diiodinated product of formula:

$I-CHR-CH_2-Z-CH_2-CHR-I$ (III)

where R and Z are defined as above;

(2) partially dehydroiodinating the product of formula (III) with a base (for instance NaOH, KOH, tertiary amines, etc.), so as to obtain the iodinated olefin of formula (I).

As to step (1), the addition of ethylene or propylene is usually carried out in the presence of suitable catalysts, such as redox systems, for instance CuI or $FeCl_3$, in solution in an organic solvent, for instance acetonitrile. The addition reaction between a perfluoroalkyliodide and an olefin is described, for instance, by M. Hudliky in "Chemistry of Organic Fluorine Compounds" (2nd Edition, Ellis Horwood Ltd., Chichester, 1976), and by R. E. Banks in "Organofluorine Chemicals and Their Industrial Applications" (Ellis Horwood Ltd, Chichester, 1979), or in J. Fluorine Chemistry, 49 (1990), 1-20 and in J. Fluorine Chemistry, 58 (1992), 1-8.

The dehydroiodination reaction of step (2) can be carried out either without any solvent, or by dissolving the diiodinated product in a suitable solvent (for instance a glycol such as diethylenglycol, or a long chain alcohol). To maximize the iodinated olefin yield, avoiding as far as possible a further dehydroiodination reaction with formation of the corresponding bis-olefin of formula CHR=CH-Z-CH=CHR, it is possible:

(a) to employ the base in defect with respect to the stoichiometric amount, with a molar ratio base/diiodinated compound preferably from 1.5 to 0.5, and then separating the iodinated olefin from the bis-olefin by fractional distillation; or

(b) to carry out the dehydroiodination reaction at reduced pressure, so as to remove the iodinated olefin from the reaction mixture as it forms, taking advantage of the fact that the latter has a boiling point lower than that of the starting diiodinated product; in such a case the reaction is preferably carried out without any solvent.

Alternatively, it is possible to carry out step (1) in defect of ethylene or propylene, to favour as much as possible formation of mono-addition product $I-Z-CH_2-CHR-I$ (which can be separated from the di-addition product by fractional distillation); the mono-addition product is then dehydroiodinated as described above, with formation of olefin I-Z-CH=CHR, which is finally submitted to a further addition of ethylene or propylene to give the iodinated olefin $I-CHRCH_2-Z-CH=CHR$.

When Z is a (per)fluoroalkylene radical, optionally containing one or more ether oxygen atoms, the starting diiodinated compound I-Z-I can be obtained by telomerization of a (per)fluoroolefin C_2-C_4 or of a (per)fluorovinylether C_3-C_8 (for instance tetrafluoroethylene, perfluoropropene, vinylidene fluoride, perfluoromethylvinylether, perfluoropropylvinylether. or mixtures thereof), by using a product of formula $I-(R_f)_k-I$ (where $k = 0, 1$; $R_f = C_1-C_8$ (per)fluoroalkylene radical) as telogenic agent. Telomerization reactions of this type are described, for instance, by C. Tonelli and V. Tortelli in J. Fluorine Chem., 47 (1990), 199, or also in EP-200,908.

When Z is a (per)fluoropolyoxyalkylene radical, the preparation of the products I-Z-I is described, for instance, in US Patent 3,810,874.

The amount of monomeric units deriving from the iodinated olefin of formula (I) present in the fluoroelastomers object of the present invention is generally from 0.01 to 1.0 moles, preferably from 0.03 to 0.5 moles, even more preferably from 0.05 to 0.2 moles, per 100 moles of the other basic monomeric units.

The total iodine amount in the fluoroelastomers object of the present invention is, on the average, from 1.8 to 5.0, preferably from 2.0 to 4.0, iodine atoms per chain. The average number of iodine atoms per chain in terminal position is in turn generally from 1.0 to 2.0, preferably from 1.5 to 1.8. The iodine atoms in terminal position can be introduced, as described in US Patent 4,243,770, by adding during polymerization iodinated chain transfer agents, such as for instance compounds of formula R_fI_x, wherein R_f is a (per)-fluoroalkyl or a (per)fluorochloroalkyl having from 1 to 8 carbon atoms, while x is 1 or 2. In particular, the iodinated chain transfer agent can be selected from: 1,3-diiodoperfluoropropane, 1,4-diiodoperfluorobutane, 1,6-diiodoperfluorohexane, 1,3-diiodo-2-chloroperfluoropropane, 1,2-di(iododifluoromethyl)-perfluorocyclobutane, monoiodoperfluoroethane, monoiodoperfluorobutane, 2-iodo-1-hydroperfluoroethane, etc. Particualrly preferred are diiodinated chain transfer agents (x=2). Alternatively, it is possible to use as chain transfer agents alkali or alkaline-earth metal iodides, as described in US Patent 5,173,553. The amount of chain transfer agent to be added to the reaction medium is chosen according to the molecular weight which is intended to be obtained and to the chain transfer agent effectiveness.

The basic structure of the fluoroelastomers object of the present invention can be selected in particular from:

(1) VDF-based copolymers, where VDF is copolymerized with at least a comonomer selected from: perfluoroolefins C_2-C_8, such as tetrafluoroethylene (TFE), hexafluoropropene (HFP); C_2-C_8 chloro- and/or bromo-fluoroolefins, such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene; (per)-

fluoroalkylvinylethers (PAVE) $CF_2=CFOR_f$, wherein R_f is a C_1-C_6 (per)fluoroalkyl, for instance trifluoromethyl, bromodifluoromethyl, pentafluoropropyl; (per)fluoro-oxyalkylvinylethers $CF_2=CFXO$, where X is a C_1-C_{12} perfluoro-oxyalkyl having one or more ether groups, for instance perfluoro-2-propoxy-propyl; C_2-C_8 non-fluorinated olefins (Ol), for instance ethylene and propylene; typical compositions are the following: (a) VDF 45-85%, HFP 15-45%, TFE 0-30%; (b) VDF 50-80%, PAVE 5-50%, TFE 0-20%; (c) VDF 20-30%, Ol 10-30%, HFP and/or PAVE 18-27%, TFE 10-30%;

(2) TFE-based copolymers, where TFE is copolymerized with at least a comonomer selected from: (per)-fluoroalkylvinylethers (PAVE) $CF_2=CFOR_f$, where R_f is defined as above; (per)fluoro-oxyalkylvinylethers $CF_2=CFOX$, wherein X is defined as above; C_2-C_8 fluoroolefins containing hydrogen and/or chlorine and/or bromine atoms; C_2-C_8 non-fluorinated olefins (Ol); typical compositions are the following: (d) TFE 50-80%, PAVE 20-50%; (e) TFE 45-65%, Ol 20-55%, VDF 0-30%; (f) TFE 32-60%, Ol 10-40%, PAVE 20-40%; (g) TFE 33-75%, PAVE 15-45%, VDF 10-22%.

The preparation of the fluoroelastomers object of the present invention can be carried out by copolymerization of the monomers in aqueous emulsion according to methods well known in the art, in the presence of radical initiators (for instance alkali metal or ammonium persulphates, perphosphates, perborates or percarbonates), optionally in combination with ferrous, cuprous or silver salts or other easily oxidable metals. In the reaction medium are usually present also surfactants of various types, among which particularly preferred are the fluorinated surfactants of formula:

$R_f\text{-}X^- M^+$

wherein R_f is a C_5-C_{16} (per)fluoroalkyl chain or a (per)fluoropolyoxyalkylene chain, X^- is $-COO^-$ or $-SO_3^-$, M^+ is selected from: H^+, NH_4^+, alkali metal ion. Among the most commonly used, we can cite: ammonium perfluorooctanoate, (per)fluoropolyoxyalkylenes terminated with one or more carboxyl groups, etc.

In a preferred embodiment, the fluoroelastomers object of the present invention are prepared in the presence of an aqueous microemulsion of perfluoropolyoxyalkylenes, as described in US Patent 4,864,006, or in the presence of an aqueous microemulsion of fluoropolyoxyalkylenes having hydrogenated end groups and/or hydrogenated repetitive units, as described in EP-625,526.

The amount of iodinated olefin of formula (I) to be added to the reaction mixture depends on the amount of units deriving therefrom which are intended to be obtained in the final product, bearing in mind that, at the low amounts employed according to the purposes of the present invention, practically the whole amount of the iodinated olefin present in the reaction medium enters the chain.

The polymerization reaction is generally carried out at a temperature of from 25° to 150°C, at a pressure up to 10 MPa.

When polymerization is completed, the fluoroelastomer is isolated from the emulsion by means of conventional methods, such as coagulation by addition of electrolytes or by cooling.

The peroxide curing is carried out, according to the art, by addition of a suitable peroxide capable of generating radicals by heating. Among the most commonly used we can cite: dialkylperoxides, such as for instance di-tertbutyl-peroxide and 2,5-dimethyl-2,5-di(tertbutylperoxy)hexane; dicumyl peroxide; dibenzoyl peroxide; ditertbutyl perbenzoate; di[1,3-dimethyl-3-(tertbutyl-peroxy)butyl]carbonate. Other peroxide systems are described, for instance, in EP Patents 136,596 and 410,351.

To the cure mixture other products are then added, such as:

(a) curing coagents, in an amount generally from 0.5 to 10%, preferably from 1 to 7%, by weight with respect to the polymer; among them commonly used are: triallyl-cyanurate; triallyl-isocyanurate (TAIC); tris (diallylamine)-s-triazine; triallylphosphite; N,N-diallylacrylamide; N,N,N',N'-tetraallyl-malonamide; trivinyl-isocyanurate; 2,4,6-trivinyl-methyltrisiloxane, etc.; TAIC is particularly preferred.

(b) a metal compound, in an amount of from 1 to 15%, preferably from 2 to 10%, by weight with respect to the polymer, selected from divalent metal oxides or hydroxides, such as for instance Mg, Zn, Ca or Pb, optionally associated to a weak acid salt, such as for instance Ba, Na, K, Pb, Ca stearates, benzoates, carbonates, oxalates, or phosphites;

(c) other conventional additives, such as fillers, pigments, antioxidants, stabilizers, and the like.

As said above, the fluoroelastomers object of the present invention do not require long post-curing treatments; to remove possible volatile by-products, after curing it is sufficient to treat the product in air for 30-60 minutes at 180°-230°C. As demonstrated by the experimentation carried out by the Applicant, longer post-curing periods do not lead to any significant improvement of mechanical and/or elastic properties of the product. This allows to drastically reduce processing times, with consequent increase of productivity for molding processes on an industrial scale.

The present invention will be now better illustrated by the following working examples, whose purpose is merely indicative but not limitative of the scope of the invention itself.

EXAMPLE 1

Preparation of $CH_2=CH-(CF_2CF_2)_3-CH_2CH_2I$.

(1) Ethylene addition

In a 5 l AISI 316 steel reactor, equipped with a magnetic stirrer, previously evacuated and then brought to nitrogen atmosphere, were loaded: 1200 g (2.17 moles) of $I-(CF_2CF_2)_3-I$ (prepared as described in J. Fluorine Chemistry, 47 (1990), 199); 12.4 g of CuI; 2.2 l of acetonitrile. The reactor was then pressurized with 5.0 moles of ethylene, and brought to a temperature of 160°C, and kept at such temperature for 10 hours under stirring. The pressure reached a maximum of 51 ate and then gradually decreased up to 10 ate. The reactor was then cooled down to room temperature, and the unreacted ethylene was discharged. The reaction mixture, containing sediments, was discharged and, after pre-stirring with excess of water, filtered on a buchner at reduced pressure, and washed with water. The collected solid was dried in an oven at 110°C. 1300 g of product were so obtained, which at gaschromatographic analysis showed a sole peak (yield: 98%).
^{19}F-NMR and ^1H-NMR analysis gave the following results:

$(I-CH^e_2CH^d_2-CF^a_2CF^b_2CF^c_2)_2$

^{19}F-NMR ($CDCl_3$)	a = -114.5 ppm; b = -123 ppm; c = -121 ppm; a/b/c = 1/1/1
^1H-NMR	e = 2.7 - 3.0 ppm; d = 3.4 ppm; e/d = 1/1.

(2) Dehydroiodination

In a 500 ml glass reactor, equipped with a mechanical stirrer, a thermometer, a dropping funnel with compensator, a water-cooled claisen with a gathering flask kept at -15°C (cold trap) were loaded: 80 g (0.131 moles) of $I-CH_2CH_2(CF_2CF_2)_3-CH_2CH_2I$ and 80 ml of diethylenglycol. The pressure in the system was reduced to 50 mmHg by means of a mechanical pump and the temperature brought to 130°C by immersion in an oil bath. A solution consisting of 15 g of NaOH dissolved in 50 ml of H_2O was then gradually added (in about 30 min). Development of vapours, which condensed in the cold trap, revealed immediately that the reaction took place. At the end of the reaction, two phases were present in the cold trap, which were separated in a separating funnel. The aqueous phase was extracted with methylene chloride, which was then removed by distillation at reduced pressure. The so obtained organic phase and that left in the reactor were put together to give a total of 52.3 g of reaction products. By means of gaschromatography analysis, the mixture resulted to be formed by:

$CH_2=CH-(CF_2CF_2)_3-CH=CH_2$	54% by weight
$I-CH_2CH_2-(CF_2CF_2)_3-CH=CH_2$	40% by weight
$I-CH_2CH_2-(CF_2CF_2)_3-CH_2CH_2-I$	6% by weight

After fractional distillation, 20.3 g of iodinated olefin $I-CH_2CH_2-(CF_2CF_2)_3-CH=CH_2$ (purity: 99%; yield: 32%) were obtained.

Polymerization reaction

In a 5 l autoclave equipped with a stirrer working at 630 rpm, were charged, after evacuation, 3.5 l of demineralized water and 36 ml of a microemulsion obtained by mixing:

- 7.8 ml of an acid terminated perfluoropolyoxyalkylene of formula:

$$CF_3O(CF_2-CF(CF_3)O)_n(CF_2O)_mCF_2COOH$$

  where n/m = 10, having average molecular weight of 600;
- 8.9 ml of a 30% by volume NH_4OH aqueous solution;

- 15.6 ml of demineralized water;
- 4.8 ml of Galden(R) D02 of formula:

$CF_3O(CF_2-CF(CF_3)O)_n(CF_2O)_mCF_3$

wherein n/m = 20, having average molecular weight of 450.

The autoclave was then brought to 80°C and kept at such temperature for the whole duration of the reaction. The following mixture of monomers was then fed:

VDF	24.0% by moles
HFP	59.5% by moles
TFE	16.5% by moles

so as to bring the pressure to 25 bar.

In the autoclave were then introduced:

- 112 ml of an aqueous solution of ammonium persulphate (APS) having a concentration of 1 g/l;
- 1,6-diiodoperfluorohexane ($C_6F_{12}I_2$) as chain transfer agent, in the form of a solution obtained dissolving 6.0 ml of the iodinated product in 14.0 ml of the same Galden(R) D02 used for the microemulsion; the addition was carried out in 20 portions, each portion of 1.0 ml, at the polymerization start and for each 5% increase in the monomer conversion;
- the iodinated olefin of formula $CH_2=CH-(CF_2CF_2)^3-CH_2CH_2I$, in the form of a solution obtained dissolving 3.0 ml in 47.0 ml of the same Galden(R) D02 described above; the addition was carried out in 20 portions, each portion of 2.5 ml, at the polymerization start and for each 5% increase in the monomer conversion.

The pressure of 25 bar was kept constant for the whole duration of the polymerization by feeding a mixture consisting of:

VDF	50% by moles
HFP	26% by moles
TFE	24% by moles.

After 300 minutes of reaction, the autoclave was cooled, the latex drained and the polymer coagulated by addition of an aluminum sulphate solution (6 g of sulphate per liter of latex). After washing, the so obtained product was dried in an oven for 24 hours at 70°C. 1500 g of product were so obtained, which was characterized as reported in Table 1. The polymer monomer composition was determined by ^{19}F-NMR analysis, the iodine percentage by X-ray fluorescence measurements. The osmometric average molecular weight (M_n^{osm}) was calculated, by calibration curves, from molecular weight values measured by Gel Permeation Chromatography (GPC).

The polymer was then peroxide cured: the vulcanization mixture composition and the characteristics of the cured product are reported in Table 2. It is to be noticed that, differently from the products of the prior art, a prolonged post-curing treatment (24 hours at 200°C) did not lead to any improvement of mechanical and elastic properties of the cured product if compared with a shorter treatment (only 1 hour at 200°C).

EXAMPLE 2

Example 1 was repeated, except that during the polymerization step 6 ml of the same iodinated olefin, dissolved in 94 ml of the same Galden(R) D02 were introduced in the reactor. The addition was carried out in 20 portions of 5 ml, at the reaction start and each 5% increase in the monomer conversion. The reaction was discontinued by cooling after 303 minutes, obtaining 1300 g of polymer. The characteristics of the product as such and after peroxide curing are reported in Tables 1 and 2, respectively.

EXAMPLE 3 (comparative)

Following the same procedure as described in Example 1, a polymer of the same type but without the iodinated olefin was prepared. The properties of the product as such and after peroxide curing are reported in Tables 1 and 2, respectively.

TABLE 1

EXAMPLE		1	2	3(*)
Polymer composition (%mole)				
VDF		53.9	55.6	54.0
HFP		20.3	19.9	21.5
TFE		25.9	24.5	24.5
iodinated olefin		0.06	0.13	--
Total iodine	(% weight)	0.29	0.41	0.22
	(per chain)	1.83	2.23	1.38
Mooney Viscosity (ASTM D1646) ML(1+10') 121°C		46	32	45
M_n^{osm}		80,000	69,000	80,000
T_g onset (°C) (DSC - ASTM D3418-82)		-13.4	-13.5	-12.0

(*) comparative

TABLE 2

EXAMPLE		1	2	3(*)
Vulcanization mixture composition				
Polymer	(g)	100	100	100
Luperco(R) 101 XL	(phr)	3	3	3
Drimix(R) TAIC	(")	4	4	4
ZnO	(")	5	5	5
Carbon black MT	(")	30	30	30
Vulcanization mixture characteristics				
*Mooney Viscosity $ML(1+10')^{121°C}$ (ASTM D1646)		45	33	41
*ODR 177°C arc 3, 12' (ASTM D2084-81)				
ML	(pounds·inch)	11	7	10
MH	(")	141	147	124
t_{s2}	(sec)	51	51	57
t_{s50}	(")	81	81	93
t'_{90}	(")	117	114	115
V_{max}	(pounds·foot·inch/sec)	2.66	3.17	2.7
Characteristics after curing in press at 170°C for 10' (ASTM D412-83)				
Modulus at 100%	(MPa)	4.8	4.5	3.6
Stress at break	(MPa)	17.3	16.7	17.2
Elongation at break	(%)	226	215	295
Shore A hardness	(points)	69	71	72
Characteristics after post-curing in oven at 200°C for 1 hour				
*MECHANICAL PROPERTIES (ASTM D412-83)				
Modulus at 100%	(MPa)	6.5	6.8	4.9
Stress at break	(MPa)	21.2	20.4	20.7
Elongation at break	(%)	205	196	273
Shore A hardness	(points)	72	74	72
*COMPRESSION SET (at 200°C for 70 hours - ASTM D395 Method B)				
O-ring 214	(%)	19	18	27
Characteristics after post-curing in oven at 200°C for 24 hours				
*MECHANICAL PROPERTIES (ASTM D412-83)				
Modulus at 100%	(MPa)	6.8	7.3	4.7
Stress at break	(MPa)	21.1	20.0	19.2
Elongation at break	(%)	198	192	272
Shore A hardness	(points)	72	74	72
*COMPRESSION SET (at 200°C for 70 hours - ASTM D395 Method B)				
O-ring 214	(%)	18	18	30

(*) comparative

EXAMPLE 4

In a 10 l autoclave, equipped with a stirrer working at 545 rpm, were loaded, after evacuation, 6.7 l of demineralized water and 66.9 ml of a microemulsion obtained by mixing:

- 14.5 ml of an acid terminated perfluoropolyoxyalkylene of formula:

$$CF_3O(CF_2\text{-}CF(CF_3)O)_n(CF_2O)_mCF_2COOH$$

wherein n/m = 10, having average molecular weight of 600;

- 14.5 ml of a 30% by volume NH_4OH aqueous solution;
- 29.0 ml of demineralized water;
- 8.9 ml of Galden(R) D02 of formula:

$CF_3O(CF_2\text{-}CF(CF_3)O)_n(CF_2O)_mCF_3$

wherein n/m = 20, having average molecular weight of 450.

The autoclave was then brought to 80°C and kept at such temperature for the whole duration of the reaction. The following monomer mixture was then fed:

VDF	64.5% by moles
MVE	32.0% by moles
TFE	3.5% by moles
(MVE = perfluoromethylvinylether)	

so as to bring the pressure to 25 bar.

In the autoclave were then introduced:

- 214 ml of a ammonium persulphate aqueous solution (APS) having concentration of 1 g/l;
- 1,6-diiodoperfluorohexane ($C_6F_{12}I_2$) as chain transfer agent, in the form of a solution obtained by dissolving 7.6 ml of the iodinated product in 12.4 ml of the same Galden(R) D02 used for the microemulsion;
- the iodinated olefin of formula $CH_2{=}CH\text{-}(CF_2CF_2)_3\text{-}CH_2CH_2I$, in the form of a solution obtained by dissolving 5.0 ml in 95.0 ml of the same Galden(R) D02 described above; the addition was carried out in 20 portions, each portion of 5 ml, at the polymerization start and each 5% increase in monomer conversion.

The pressure of 25 bar was kept constant for the whole duration of the polymerization by feeding a mixture consisting of:

VDF	75% by moles
MVE	21% by moles
TFE	4% by moles.

After 187 minutes of reaction, the autoclave was cooled, the latex drained and the polymer coagulated by addition of an aluminum sulphate solution (6 g of sulphate per liter of latex). After washing, the so obtained product was dried in an oven for 24 hours at 70°C. 2500 g of product were so obtained, which was characterized as reported in Table 3.

The polymer was then peroxide cured: the vulcanization mixture composition and the characteristics of the cured product are reported in Table 4.

EXAMPLE 5 (comparative)

Following the same procedure as described in Example 4, a polymer of the same type but without the iodinated olefin was prepared. The properties of the product as such and after peroxide curing are reported in Tables 3 and 4 respectively.

TABLE 3

EXAMPLE		4	5(*)
Polymer composition (%mole)			
VDF		79.0	80.2
HFP		17.0	15.7
TFE		4.0	4.0
iodinated olefin		0.05	--
Total iodine	(% peso) (per chain)	0.30 1.53	0.26 1.31
Mooney viscosity (ASTM D1646)			
ML(1+10') 121 °C		28	28
ML(1+4') 100 °C		52	58
M_n^{osm}		65,000	64,000
T_g onset (°C) (DSC - ASTM D3418-82)		-36.1	-37.0

(*) comparative

TABLE 4

EXAMPLE		4	5(*)
Vulcanization mixture composition			
Polymer	(g)	100	100
Luperco(R) 101 XL	(phr)	3	3
Drimix(R) TAIC	(")	4	4
ZnO	(")	5	5
Carbon black MT	(")	30	30
Vulcanization mixture characteristics			
*Mooney Viscosity $ML(1+10')^{121°C}$ (ASTM D1646)		30	33
*ODR 177°C arc 3, 12' (ASTM D2084-81)			
ML	(pounds·inch)	7	7
MH	(")	134	113
t_{s2}	(sec)	51	57
t_{s50}	(")	81	87
t'_{90}	(")	111	114
V_{max}	(pounds·foot·inch/sec)	3.3	2.85
Characteristics after curing in press at 170°C for 10' (ASTM D412-83)			
Modulus at 100%	(MPa)	3.4	2.6
Stress at break	(MPa)	14.5	13.5
Elongation at break	(%)	236	324
Shore A hardness	(points)	66	64
Characteristics after post-curing in oven at 200°C for 1 hour			
*MECHANICAL PROPERTIES (ASTM D412-83)			
Modulus at 100%	(MPa)	3.6	2.9
Stress at break	(MPa)	16.3	15.5
Elongation at break	(%)	237	292
Shore A hardness	(points)	67	66
*COMPRESSION SET (at 200°C for 70 hours - ASTM D395 Method B)			
O-ring 214	(%)	24	36
Characteristics after post-curing in oven at 200°C for 24 hours			
*MECHANICAL PROPERTIES (ASTM D412-83)			
Modulus at 100%	(MPa)	6.8	4.7
Stress at break	(MPa)	21.1	19.2
Elongation at break	(%)	198	272
Shore A hardness	(points)	72	72
*COMPRESSION SET (at 200°C for 70 hours - ASTM D395 Method B)			
O-ring 214	(%)	22	33

(*) comparative

Claims

1. Peroxide curable fluoroelastomers, having iodine atoms in terminal position, and monomeric units in the chain deriving from an iodinated olefin of formula:

   $CHR=CH\text{-}Z\text{-}CH_2CHR\text{-}I$ (I)

wherein: R is -H or $-CH_3$; Z is a C_1-C_{18} (per) fluoroalkylene radical, linear or branched, optionally containing one or more ether oxygen atoms, or a (per)fluoropolyoxyalkylene radical.

2. Fluoroelastomers according to claim 1, wherein in formula (I) Z is a C_4-C_{12} perfluoroalkylene radical.

3. Fluoroelastomers according to claim 1, wherein in formula (I) Z is a (per)fluoropolyoxyalkylene radical of formula:

$$-(Q)_p-CF_2O-(CF_2CF_2O)_m(CF_2O)_n-CF_2-(Q)_p- \quad (II)$$

wherein: Q is a C_1-C_6 alkylene or oxyalkylene radical; p is 0 or 1; m and n are numbers such that the ratio m/n is from 0.2 to 5 and the molecular weight of said (per)fluoropolyoxyalkylene radical is from 400 to 10,000.

4. Fluoroelastomers according to claim 3, wherein Q is selected from: $-CH_2O-$; $-CH_2OCH_2-$; $-CH_2-$; $-CH_2CH_2-$.

5. Fluoroelastomers according to anyone of the previous claims, wherein the amount of units deriving from the iodinated olefin of formula (I) is from 0.01 to 1.0% by mole per 100 moles of the other basic monomeric units.

6. Fluoroelastomers according to claim 5, wherein the amount of units deriving from the iodinated olefin of formula (I) is from 0.03 to 0.5% by mole per 100 moles of the other basic monomeric units.

7. Fluoroelastomers according to anyone of the previous claims, wherein the average number of iodine atoms per chain in terminal position is from 1.0 to 2.0.

8. Fluoroelastomers according to claim 7, wherein the average number of iodine atoms per chain in terminal position is from 1.5 to 1.8.

9. Fluoroelastomers according to anyone of the previous claims, wherein the total amount of iodine atoms per chain is, on the average, from 1.8 to 5.0.

10. Fluoroelastomers according to any of the previous claims, wherein the total amount of iodine atoms per chain is, on the average, from 2.0 to 4.0.

11. Fluoroelastomers according to claim 1, wherein the monomeric structure is based on vinylidene fluoride (VDF), copolymerized with at least a comonomer selected from: C_2-C_8 perfluoroolefins; chloro- and/or bromofluoroolefins C_2-C_8; (per)fluoroalkylvinylethers (PAVE) $CF_2=CFOR_f$, where R_f is a C_1-C_6 (per)-fluoroalkyl; (per)fluoro-oxyalkylvinylethers $CF_2=CFOX$, where X is a C_1-C_{12} (per)fluoro-oxyalkyl having one or more ether groups; C_2-C_8 non-fluorinated olefins (Oℓ).

12. Fluoroelastomers according to claim 11, wherein the basic monomeric structure is selected from: (a) VDF 45-85%, HFP 15-45%, TFE 0-30%; (b) VDF 50-80%, PAVE 5-50%, TFE 0-20%; (c) VDF 20-30%, Oℓ 10-30%, HFP and/or PAVE 18-27%, TFE 10-30%.

13. Fluoroelastomers according to claim 1, wherein the monomeric structure is based on tetrafluoroethylene (TFE), copolymerized with at least a comonomer selected from: (per)-fluoroalkylvinylethers (PAVE) $CF_2=CFOR_f$, where R_f is a C_1-C_6 (per)fluoroalkyl; perfluorooxyalkyl-vinylethers $CF_2=CFOX$, where X is a C_1-C_{12} (per)fluorooxyalkyl having one or more ether groups; C_2-C_8 fluoroolefins containing hydrogen and/or chlorine and/or bromine atoms; C_2-C_8 non-fluorinated olefins (Oℓ).

14. Fluoroelastomers according to claim 13, wherein the basic monomeric structure is selected from: (d) TFE 50-80%, PAVE 20-50%; (e) TFE 45-65%, Oℓ 20-55%, VDF 0-30%; (f) TFE 32-60%, Oℓ 10-40%, PAVE 20-40%; (g) TFE 33-75%, PAVE 15-45%, VDF 10-22%.

15. Fluoroelastomers according to anyone of the previous claims, obtainable by a copolymerization process of the monomers in aqueous emulsion in the presence of a radical initiator and of an iodinated chain transfer agent.

16. Fluoroelastomers according to claim 15, wherein the iodinated chain transfer agent is a compound of formula R_fI_x, wherein R_f is a (per)fluoroalkyl or a (per)fluorochloroalkyl having from 1 to 8 carbon atoms, while x is 1 or 2.

17. Fluoroelastomers according to claim 15 or 16, wherein the copolymerization process of the monomers is carried out in the presence of an aqueous microemulsion of perfluoropolyoxyalkylenes or of fluoropolyoxyalkylenes having hydrogenated end groups and/or hydrogenated repetitive units.

18. Iodinated olefins of formula (I), defined according to claims from 1 to 4.

19. Process for preparing the iodinated olefins of claim 18, which comprises in sequence:
(1) adding ethylene or propylene to a compound of formula I-Z-I, to obtain a diiodinated product having the formula:

$$I\text{-}CHR\text{-}CH_2\text{-}Z\text{-}CH_2\text{-}CHR\text{-}I \qquad (III)$$

wherein R and Z are defined as above;
(2) partially dehydroiodinating the product of formula (III) with a base so as to obtain the iodinated olefin of formula (I).

20. Process according to claim 19, wherein step (2) is carried out in defect of the base, and afterwards the iodinated olefin is separated by fractional distillation.

21. Process according to claim 19, wherein the step (2) is carried out at reduced pressure, so as to remove the iodinated olefin from the reaction mixture as it forms.

22. Process according to claim 19, wherein step (1) is carried out in defect of ethylene or propylene, so as to favour formation of mono-addition product $I\text{-}Z\text{-}CH_2\text{-}CHR\text{-}I$; the mono-addition product is then dehydroiodinated according to step (2), with formation of the olefin $I\text{-}Z\text{-}CH{=}CHR$, which is finally subjected to futher addition of ethylene or propylene to give the iodinated olefin of formula (I).

23. Use of the fluoroelastomers according to claims from 1 to 16 for manufacturing O-rings.

24. Use according to claim 23, wherein the fluoroelastomers have basic monomeric composition according to claim 14.

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(54) **New peroxide curable fluoroelastomers, particularly suitable for manufacturing O-rings**

(57) New fluoroelastomers are described, having iodine atoms in terminal position and monomeric units in the chain deriving from an iodinated olefin of formula:

$$CHR{=}CH\text{-}Z\text{-}CH_2CHR\text{-}I \qquad (I)$$

wherein: R is -H or $-CH_3$; Z is a (per)fluoroalkylene radical C_1-C_{18}, linear or branched, optionally containing one or more ether oxygen atoms, or a (per)fluoropolyoxyalkylene radical.

These products, upon peroxide curing, require extremely short post-curing treatments (around 30-60 minutes at 180°-230°C) and are characterized by compression set values lower than 25% (measured on O-rings at 200°C for 70 hours according to ASTM Standard D395 Method B).

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EUROPEAN SEARCH REPORT

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EP 95 10 7005

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X Y Y	US-A-5 231 154 (HUNG) * claims; example 7; tables *	1 1-22 23,24	C07C21/18 C08F214/18
Y	US-A-4 612 357 (BEKIARIAN ET AL.) * column 2, line 66 - column 3, line 11 *	1-22	
Y	FR-A-1 410 444 (DU PONT DE NEMOURS) * examples 6,12 *	1-22	
Y	US-A-5 151 492 (ABE ET AL.) * column 2, line 50 - line 54; claims; example 4 *	23,24	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C07C
C08F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 November 1995	Loiselet-Taisne, S

CATEGORY OF CITED DOCUMENTS

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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid,

namely claims:

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,
namely:

see sheet -B-

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respects of which search fees have been paid,

namely claims:

☐ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims,

namely claims:

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EP 95 10 7005 -B-

LACK OF UNITY OF INVENTION - A PRIORI -

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims 1-22: Iodinated olefins of formula (I)
2. Claims 23-24: Use of peroxide curable fluoroelastomers having monomer of formula (I)